PROCEEDINGS OF THE IV INTERNATIONAL CONFERENCE/HIGH TEMPERATURE CAPILLARITY
JOURNAL OF MATERIALS SCIENCE **40** (2005) 2459–2463

Wetting and mechanical properties, a case study: Liquid metal embrittlement of a martensitic steel by liquid lead and other liquid metals

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We present experimental results of tensile and fatigue properties of the T91 (a 9% Cr martensitic steel) in a stagnant molten metallic bath (Pb, Pb-Bi or Sn for instance). Under particular experimental conditions, the tensile tests revealed an instantaneous embrittlement of the material, more pronounced at low temperature, that disappears as the temperature is raised above 450°C. This behavior is explained by the reduction of the surface energy of the bare metal induced by the adsorption of the liquid metal. When the steel is submitted to low cycle fatigue tests in presence of the liquid Pb-Bi eutectic at 300°C, its lifetime is significantly reduced compared to tests performed in air. In this case, given the complexity of the mechanisms leading to a fatigue fracture, it is more difficult to ascribe the observed embrittlement to the sole surface-energy reduction effect, but and adsorption-induced localization of the plastic deformation at the very crack tip is an appealing hypothesis.

1. Introduction

The understanding of the influence of a liquid metal environment on the mechanical properties of structural materials is a major issue for many high temperature applications. The presence of a liquid metal can induce accelerated corrosion in some cases and grain boundary penetration in others. Both mechanisms involve mass transport and thermally activated processes and have detrimental effects. In this article we will address a third possible cause of degradation due to an instantaneous adsorption-induced decrease of the surface energy, γ_s, known as the Rehbinder effect [1]. While it is clear from the Griffith criterion of brittle crack propagation that a reduction of γ_s should entail a reduction of the material toughness, its consequences on the mechanical properties of ductile materials submitted to tensile and cyclic loading is less obvious. In this article, we present a case study of liquid metal embrittlement that involves liquid lead or lead alloys and the martensitic steel T91. We propose a general interpretation of experimental results already published elsewhere [2–6] based on the adsorption-induced reduction of γ_s.

The article is organized as follows: we first describe the experimental procedures and then the results are summarized. In the discussion we recall some ideas about the brittle fracture of ductile materials and we indicate some possible effects of the liquid metal on the tensile and fatigue properties.

2. Experimental procedure

2.1. Base material

The base material, the Z10 CD Nb V 9-1 (AFNOR) steel or Grade 91 (T91) was supplied by Creusot Loire Industries. Its standard chemical composition is given in Table I. The as-received material, after being submitted to the standard heat treatment consisting in heating for one hour at 1050°C, air quenching, heating for one hour at 750°C and then air cooling, has a tempered martensitic microstructure. Due to its low carbon content, its crystallographic structure is bcc and the average grain size is about 20 μm [2, 3].

2.2. Specimen preparation, tensile and fatigue tests and fractography

Cylindrical tensile specimens with a 4 mm diameter and a gauge length of 20 mm were machined from the as received ingots. In order to increase as much as possible the steel hardness, a specific heat treatment was applied consisting in tempering the steel at 500°C instead of 750°C [2]. This changed neither the crystallographic structure nor the grain size (which is only controlled by the austenitization treatment). In some specimens, a notch (depth = 500 μm, curvature radius = 200 μm) was mechanically machined.

The tensile tests were performed at constant stroke speed corresponding to a strain rate of 10^{-4} s^{-1} using a

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TABLE I Chemical composition of the steel 91 used in this work

Major elements	Cr	Mo	V	Mn	Si	Ni	C	Nb	Fe
Weight (%)	8.80	1.00	0.25	0.38	0.41	0.17	0.11	0.07	balance

Schenck RMC 100 servo-electric test machine. For the high-temperature tests, a standard three zone furnace was used. No particular oxygen activity control was performed and a stagnant liquid metal bath was used.

To study the effect of a liquid metal on the fatigue properties, low cycle fatigue experiments have been carried out using the T91 steel submitted to the standard heat treatment (i.e. tempering at 750°C). The specimens were smooth and cylindrical with a gauge length of 10 mm and a gauge diameter of 10 mm. Their surface was carefully electropolished in order to avoid any effect of surface roughness on the fatigue life. Tests at 300°C were performed in air and in a liquid Pb-Bi (56 at.%Pb–44 at.%Bi) alloy using a servo-hydraulic MTS machine with a load capacity of 100 kN.

The fatigue tests were carried out in a fully push-pull mode ($R_\varepsilon = -1$) at three imposed total strain amplitudes $\Delta\varepsilon_t$ (2.2%, 1.6%, 0.6%). An extensometer for strain control, a triangular wave and a constant strain rate of 4×10^{-3} s^{-1} (corresponding to loading frequencies of 0.09, 0.125 and 0.33 Hz respectively) were used. During cycling, hysteresis loops were periodically recorded, measuring the stress variation amplitude $\Delta\sigma$ for each cycle.

A FEI Quanta 400 scanning electron microscope in secondary electron mode was used to perform the fractographic analysis.

3. Results

The tensile tests revealed an embrittlement of the steel by the liquid metal only under particular conditions [2–5]: the $\sigma - \varepsilon$ curves of Fig. 1 were obtained at 350°C in liquid lead on notched samples submitted to the hardening heat treatment described in the previous paragraph. It is important to note that, before material failure, the curves obtained in air and in the liquid metal coincide. This means that the presence of the liquid metal does not modify the bulk plastic properties. A similar behaviour was observed with this steel in other liquid metal environments (Pb-Bi eutectic, Sn) at temperatures ranging between 250°C and 400°C. Fractographic analysis reveals ductile fracture with characteristic dimples for the specimens tested in air, and cleavage-like transgranular brittle fracture for the specimens tested in liquid metal (the fracture surfaces of specimens tested in liquid Sn were covered by intermetallic compounds). Inspection of the sample surfaces revealed that the machining of the notch entails the formation of a hard cold-worked surface layer ~10 μm thick, which breaks early during the tensile tests. In a liquid metal environment the microcracks thus generated propagate in a brittle manner, which does not seem to be the same in air.

By integrating the σ-ε curves, a ductility indicator is obtained, which represents the mechanical energy needed to break the samples. As shown in Fig. 2, the embrittlement effect for the T91-liquid lead case progressively disappears as the temperature is raised, a behaviour similar to that observed in standard brittle-to-ductile transitions.

Concerning the mechanical properties of the standard steel submitted to cyclic loading, the evolution of the stress amplitude $\Delta\sigma/2$ versus the number of cycles N is reported in Fig. 3 for the tests made in air at 300°C. As can be seen, the T91 steel exhibits cyclic softening

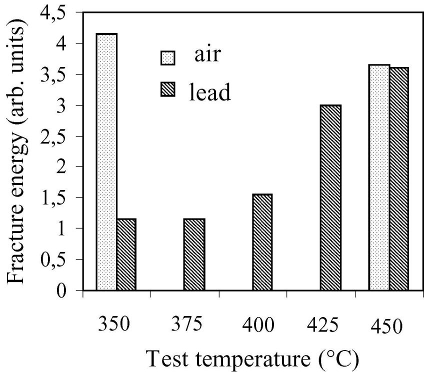

Figure 2 Ductility well determined from tensile tests similar to those of Fig. 1.

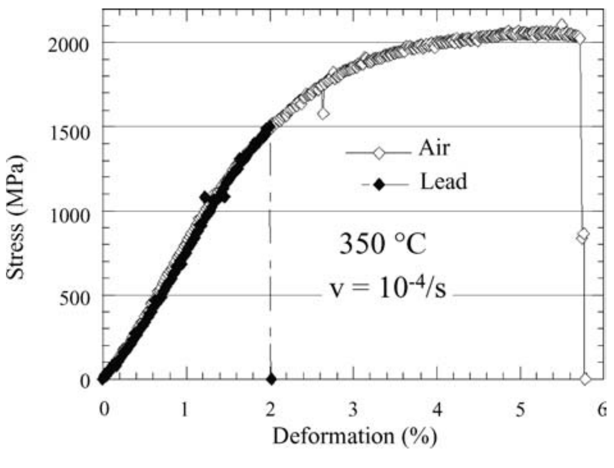

Figure 1 Tensile test curves of notched specimens submitted to a hardening heat treatment. The tests were performed at 350°C in air (open symbols) and in liquid lead (full diamonds).

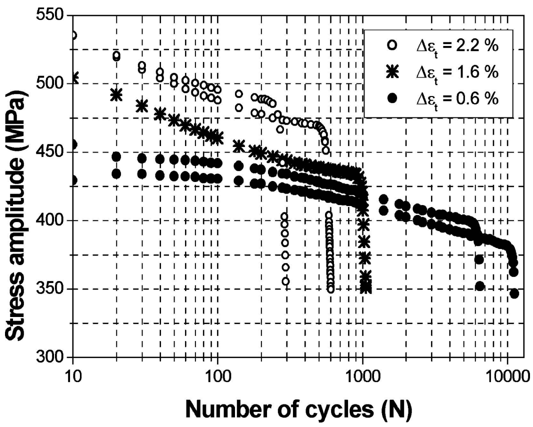

Figure 3 Evolution of the stress amplitude versus the number of cycles in air at 300°C for different strain amplitudes.

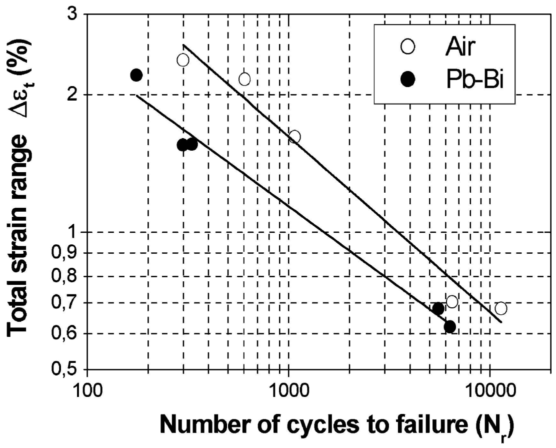

Figure 4 Fatigue resistance diagram of the T91 steel tested at 300°C in air and liquid Pb-Bi alloy.

very early in the fatigue life followed by a marked decrease of the stress amplitude associated with the propagation of a macroscopic crack into the bulk before final failure. This behaviour is typical for martensitic or ferrito-bainitic steel [8]. The same overall behaviour was observed when cycling in contact with the liquid Pb-Bi alloy: the cyclic accommodation and the stress values do not differ from what is observed in air. This indicates that, as it is the case under tensile stress, the bulk properties during fatigue tests are not modified by the presence of the liquid metal, a situation similar to that observed during corrosion-fatigue tests [9]. In spite of the resemblance, it is important to point out that, for a given strain amplitude, the fatigue life is smaller in liquid Pb-Bi than in air. As can be seen Fig. 4, were the number of cycles to failure is plotted versus the imposed strain, the fatigue resistance is reduced in the liquid metal by at least a factor of 2, a result that agrees with data reported by Kalkhof *et al.* [10] for a martensitic steel 10.5Cr- Manet-II tested in Pb-Bi at 260°C. The experimental observations suggests that the liquid metal favour crack initiation and propagation, a hypothesis that is at least partially confirmed by the transverse cross sections of the cracked samples shown Fig. 5. While the samples tested in air present numerous short cracks that develop from the surface, the specimens tested in liquid metal have only a major crack that propagates in the bulk.

4. Discussion

As mentioned in the previous section, it is very likely that the embrittlement shown by the tensile test is due to the brittle propagation in the liquid metal environment of microcracks formed during the test by the cracking of the hard coat produced by the machining of the notches. Similar microcracks also appear during the tests performed in air, but they are not able to propagate in a brittle manner in this case. Therefore, the main effect of the liquid metal is to favor the propagation of brittle cracks that otherwise (in the absence of the liquid metal) can not advance. This property can be associated to a decrease of the toughness of the material.

Unless intrinsically brittle materials like some rocks, oxides, glasses or covalent materials at low temperature are considered, the prediction of the toughness remains an intricate task since it involves different length scales, ranging from the atomic distances related to bond breaking, to some μm typical of distances between dislocations. Among ductile materials, two distinct classes can be distinguished: intrinsically ductile materials and extrinsically ductile ones [7]. Intrinsically ductile materials are those for which a crack, submitted to a mechanical loading, emits dislocation from the very crack tip instead of propagating in order to relax the mechanical energy G. If a material is an intrinsically ductile material it will remains ductile whatever the temperature. On the contrary, when a crack tip is able to propagate instead of emiting dislocations, but dislocations sources ahead of the crack tip are activated and screen the crack tip from the applied load, the material is said to be extrinsically ductile. These materials generally display a brittle-to-ductile transition as the temperature is raised. According to the well-known Rice and Thomson criteria [11], bcc metals are extrinsically ductile while fcc ones are intrinsically ductile. Since the martensitic steel T91 undergoes a brittle-to-ductile transition, it can be considered to be an extrinsically ductile material. Assuming this, we will show that the liquid metal embrittlement observed can be understood within the Griffith theory of brittle crack propagation.

Our tensile tests results clearly show the existence of a brittle-to-ductile transition as a consequence of the intimate contact between the crack tip and the liquid metal. This result can be easily understood if one assumes that in spite of significant plastic deformation ahead of the crack tip, the crack propagation

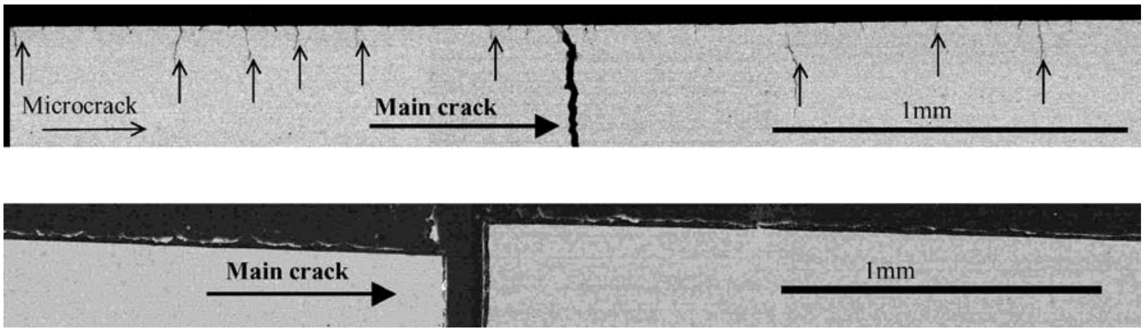

Figure 5 Transverse cross section of the specimens showing multiple microcracks besides the main crack for fatigue tests performed in air (upper figure) and an isolated main crack propagating in the bulk for fatigue tests performed in the liquid metal bath (lower figure).

occurs when the stress intensity at the crack tip K_{tip}, reaches K_G, the value predicted by the Griffith criterion for the stress intensity ($K_G \sim \sqrt{2\gamma E}$ for a Griffith crack). Although the original version of the Griffith criterion relies on the concept of the mechanical energy release rate G, an equivalence between the G_{1C} and the K_G criterion is found assuming that the crack remains sharp at the atomic scale. Recent atomic-scale simulations [12, 13] have showed, however, that the K_G criterion can be extended and remains valid to a good accuracy in spite of significant crack blunting, the major effect of the blunting being however the switch from a crack propagation to a dislocation emission behavior.

Different research groups modeling the toughness of extrinsically ductile materials and the brittle to ductile materials have adopted this point of view. For instance Roberts *et al.* [14, 15] modeled the brittle to ductile transition in the following way: dislocation sources are disposed at a distance x_c ahead of the crack tip in a given slip plane. The situation of a loading mode III and dislocations emitted in the crack plane can be treated analytically: in this case the applied stress intensity K_{III}, and its value at the crack tip K_{tip}, are related by

$$K_{\text{tip}} = K_{\text{III}} - \sum_{\text{j}} \frac{\mu b}{(2\pi x_{\text{j}})^{1/2}}$$

with x_{j}, the distance of the jth dislocation to the crack tip, μ the shear modulus and b the Burgers vector magnitude. This expression illustrates the shielding effect of the emitted dislocations. Moreover, the sources being at a distance x_c from the crack tip, the back-stresses acting on them are higher than those felt at the crack tip. As a consequence, at high enough deformation the sources could become blocked, and any subsequent increment of K_{III} would result in a K_{tip} increase. When K_{tip} reaches the K_G value, the crack propagates. This simple model can explain the origin of the brittle-to-ductile transition in some cases, and allows understanding a possible effect of the liquid metal on the materials behavior. The adsorption of liquid metals induces a decrease of γ_s, and therefore of K_G, with a value in the liquid metal $K'_G < K_G$. As a consequence, at a given temperature, the material can exhibit a brittle behavior in contact with a liquid metal (K_{tip} reaches K'_G before intense plastic deformation occurs) while it shows a ductile one in air. According to this interpretation, the main effect of the liquid metal with respect to the tensile properties of a ductile material will be a decrease of the toughness. As the temperature is increased, the shielding effect of the dislocations emitted by the sources become more efficient and may prevent K_{tip} from reaching K'_G: in this case a fully ductile fracture, as observed in air, is expected.

If the liquid metal remained liquid even at very low temperature there should be a shift of the ductile to brittle transition temperature (DBTT) towards higher T values. In the case of a melting temperature greater than the DBTT in air, a ductility well should appear between the liquid metal melting temperature and the DBTT in contact with the liquid metal, as illustrated in Fig. 2.

So far we have discussed the effect of the liquid metal adsorption assuming that the main contribution to the crack tip plasticity is due to sources located ahead of the crack tip. The adsorption of the liquid metal may also affect the capability of the crack tip to act as a dislocation source. Concerning the ductility of the crack tip, a recent development due to Rice [16] points out the importance of the γ_{uns} concept, γ_{uns} being the maximum energy per unit surface needed to translate two rigid blocks of material, one with respect to the other, along the Burgers vector. Numerical simulations at the atomic scale confirmed that when dislocation are emitted from the crack tip in slip planes that coincide with the crack plane (non-blunting dislocations) the lower γ_{uns}, the easier the emission [17]. Furthermore, the Rice criterion for dislocation emission given in the form of critical stress intensity K_e proportional to $\sqrt{\gamma_{\text{uns}}}$ was verified with an excellent accuracy by the atomic scale simulations. However, when the dislocation emission by the crack tip is made in slip planes that form an angle with the crack plane (blunting dislocations), the γ_{uns} criterion is no longer verified. Instead, criteria based on the tensile component of the stress have to be adopted [18]. The origin of this discrepancy may be attributed to the additional work needed to create surface steps when the dislocation is emitted. In the presence of adsorbed liquid metal this quantity should be lower than in air meaning that under appropriate loading conditions the crack tip could be activated as a dislocation source.

If this occurs for the fatigue microcracks of Fig. 5 (upper panel), the plastic localization may assist the small surface cracks to overcome the grain boundaries, which constitute the main structural barrier to their propagation. As their length increases the considerations exposed for the tensile crack may also come into play, the overall effect of the liquid metal being an accelerated surface crack propagation. This explanation is however a simple hypothesis that needs further investigation (currently undertaken) in order to be validated.

5. Conclusion

We have analyzed experimental results of liquid metal embrittlement of the T91 steel by liquid lead and liquid lead alloys within the framework the adsorption-induced reduction of the surface energy model known as Rehbinder effect [1]. Our analysis qualitatively explains the observed experimental facts, namely: (i) the instantaneous embrittlement effect (no solid state diffusion is needed), (ii) the progressive loss of the embrittlement as the temperature is raised and (iii) the accelerated surface crack propagation into the bulk under cycling loading that induce a significant reduction of the fatigue life.

Acknowledgements

This work has been supported by the French CNRS GdR GEDEON and GEDEPEON as well as by european projects TECLA and MEGAPIE-Test in the framework of the 5th PCRD EURATOM program.

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Received 31 March
and accepted 18 July 2004